ADSORPTION AND RELEASE OF PHOSPHATE ION BY SOILS AND CLAYS

BY

LESTER TOUBY KURTZ

B. S., Purdue University, 1938

M. S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1943

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ADSORPTION AND RELEASE OF PHOSPHATE ION BY SOILS AND CLAYS

A study was made of the reactions which take place when soluble phosphate is added to the soil and to various clays and of the chemical forms of phosphate which result from these reactions. The general procedure in the adsorption studies was to bring samples of the soils or clays into contact with solutions of known phosphate concentrations, and to determine the decrease in the amount of phosphate in solution after definite periods of time. The forms of the adsorbed phosphate were studied by determining the ease with which they could be removed by water and other extracting solutions.

It was shown that the chief reaction was definitely one of adsorption which in its initial stages at least appears to be of the polar type. The amount of phosphate adsorbed by the soil is a function of the concentration of the phosphate in solution and isotherms typical of exchange adsorption are obtained. In the cases studied, the adsorption curves appear to take a similar form for both the soils and clays, the extent of the reaction varying with the material. In many cases the adsorption may be expressed by an equation of the Freundlich type.

In the clays studied it was found that the indianaite (halloysite) and the North Carolina china clay (kaolinite) adsorbed more phosphate than the bentonite or illite clays. This behavior is in accord with the phosphate-hydroxyl exchange theory which would require the 1:1 lattice type clays to have a greater adsorbing capacity. Another kaolinitic clay, however, showed a very low adsorption capacity.

Marked differences in the ability of the different clays to hold adsorbed phosphate against water and ammonium fluoride were also found. The fluoride ion readily replaced the adsorbed phosphate from the indianaite (halloysite) and the North Carolina china clay (kaolinite) but it was relatively ineffective in removing the small amounts of adsorbed phosphate from the other clays. Water extractions were more effective than fluoride in removing phosphate from the bentonite (montmorillinite) and illite samples.

In a comparison of four different soils which are representative of large areas of Illinois, it was found that the amounts of phosphate adsorbed varied in the order Clement > Cisne < Muscatine < Sable, the Clement retaining approximately twice as much as the Sable.

Extraction of stored samples of soils to which phosphate had been added three years before recovered over ninety per cent of the added phosphate. In these extractions three fractions, namely, water extractable, ammonium fluoride extractable, and easily acid soluble were determined. In these studies it was established that there is not only an increase in phosphate adsorption with time but that there is also a change in the status of the adsorbed phosphate with time. This is shown by the decreases in the amounts of phosphate which may be removed by water in successive extractions and by the increase in the easily acid soluble fraction. The greater part of the phosphate remains in an adsorbed form from which it may be displaced by the fluoride ion.

The ability of the different anions, when compared as solutions of neutral salts, to replace phosphate from a soil which had been heavily phosphated five years before was found to be as follows: fluoride > oxalate > citrate > bicarbonate > borate > acetate > sulfate > thiocyanate > chloride. The fluoride was outstanding in this series since it quickly recovered nearly all of the added phosphate. The oxalate was also effective but its action was slower. The amounts of phosphate removed by borate were of the same order as that recovered by water. The anions below borate in the series actually depressed the amount removed as compared to water alone.

The similarities between anion and cation adsorption were discussed and an analogy between the two phenomena was developed. Some of the mechanisms which have been proposed for phosphate adsorption and the limitations and difficulties of the anion adsorption theory were discussed.

From this study the following conclusions were drawn:

1. The trend of phosphate adsorption in widely different Illinois soils is so similar that the same reactions may be assumed to be taking place and the same mechanisms of adsorption oper-

ating in all cases.

2. The form of the adsorption curves, the behavior of the adsorbed phosphate toward water extractions and the ease with which the added phosphate can be removed from the soil by water and by various anions shows that, in the initial stages at least, the phosphate reaction with soils has many characteristics of an exchange adsorption. The writer does not feel justified, however, in assuming that the adsorption is due to any single mechanism.

3. In short periods of time, the chief factor in determining the amount of phosphate adsorbed by a given material is the concentration of the phosphate solution in contact with the colloid. For a given concentration the nature of the adsorbing material is the important factor. Under the conditions of this study, variations in the pH of the solutions play a minor role in determining the amount of phosphate adsorbed.

4. The adsorption reaction is reversible to a large degree, but the reversibility decreases with time. This change of status of the adsorbed phosphate must be due to a rearrangement of forces or bonds which hold the phosphate on the clay surfaces. During this aging process, the phosphate ions are believed to form more stable combinations with the iron, aluminum, and silicon of the crystal lattice.

5. Even after long periods of time, added phosphate is still largely held in a form from which it can be readily removed by displacement by other anions which also tend to be adsorbed by the soil.

6. When small additions of phosphate are made to a soil, only small increases in the water extractable phosphate are found. Where large additions are made, the amounts of water extractable phosphate are not only larger in proportion to the amounts added, but will remain so for long periods of time.

7. The conditions in the heavily phosphated soil samples in this study are similar to those found in the immediate location in the soil where phosphate is drilled or hill-dropped in the fleld. In both cases adsorbed phosphate is high and will supply phosphate to the soil solution for long periods of time. With small

phosphate additions, the conditions are similar to those found when phosphate is broadcast in the field. Here the phosphate in solution is raised only slightly for short periods of time.

8. This study shows that "phosphate fixation" in Illinois soils does not constitute an argument against the practicability or advisability of using soluble phosphate in fertilizers and it also shows that the loss of phosphate from crop utilization because of its reactions with soil is not as serious as was formerly believed.

VITA

The writer was born Noverber 7, 1914, in Howard County, Indiana. He attended the Howard Township Consolidated School where he graduated from high school as honor student in 1933. In the fall of 1934, he entered Purdue University where he received the Bachelor of Science degree in June, 1938. In the following September, he became half-time assistant in Soils in the Department of Agronomy at the University of Illinois where he received his Master of Science degree in 1940. Since April, 1942, he has been full-time assistant in the Agronomy Department at the University of Illinois.

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